Magnetic properties of fullerene salts containing d- and f-metal cations (Co^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Eu^{2+}, Cd^{2+}). Specific features of the interaction between $C_{60}^{\bullet-}$ and the metal cations

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The interaction between the radical anions $C_{60}^{\cdot-}$ and divalent d- and f-metal (Co, Fe, Ni, Mn, Eu, Cd) cations in DMF and acetonitrile—benzonitrile (AN—BN) mixture was studied. Black solid polycrystalline salts $(C_{60}^{\cdot-})_2\{(M^{2+})(DMF)_x\}$ (x = 2.4—4, **1—6**) containing the radical anions $C_{60}^{\cdot-}$ and metal(II) cations solvated by DMF were prepared for the first time and their optical and magnetic properties were studied. The salts containing Co^{2+}, Fe^{2+}, and Ni^{2+} are characterized by antiferromagnetic interactions between the radical anions $C_{60}^{\cdot-}$, which result in unusually large broadening of the EPR signal of $C_{60}^{\cdot-}$ upon lowering the temperature (from 5.55—12.6 mT at room temperature to 35—40 mT at 6 K for Co^{2+} and Ni^{2+}). The salts containing Mn^{2+} and Eu^{2+} form diamagnetic dimers $(C_{60}^{-})_2$, which causes a jumpwise decrease in the magnetic moment of the complexes and disappearance of the EPR signal of $C_{60}^{\cdot-}$ in the temperature range 210—130 K. A feature of salt **6** is magnetic isolation of the radical anions $C_{60}^{\cdot-}$ due to the presence of diamagnetic cation Cd^{2+}. The salts prepared are unstable in air and decompose in *o*-dichlorobenzene or AN. Reactions of $C_{60}^{\cdot-}$ with metal(II) cations in AN—BN mixture result in decomposition products of the salts that contain neutral fullerene dimers and metals solvated by BN.

Key words: radical ion salts, fullerene C_{60}, metal(II) cations, magnetic properties, antiferromagnetic interactions, dimerization of $C_{60}^{\cdot-}$, EPR spectroscopy.

Ionic compounds of fullerenes exhibit superconductivity and ferromagnetism.[1—3] Of particular interest are the fullerene salts containing paramagnetic d- and f-metals, which show high conductivity or long-range magnetic order of spins. Moreover, these phenomena can coexist in a single compound.[4—7] For instance, doping C_{60} with f-metals in the gas phase led to formation of superconductors $M_{2.75} \cdot C_{60}$ (M = Yb, Sm) with the superconducting transition temperature (T_c) up to 6 K.[4,5] Doping fullerenes with europium led to a ferromagnetic phase Eu_6C_{60} with T_c = 14 K.[6] The coexistence of superconductivity and ferromagnetism in $Ce_x \cdot C_{60}$ was reported.[7] Crystalline salts containing the dianions C_{60}^{2-} and divalent metal cations $\{(M^{2+})(NH_3)_{6(7)}\}(C_{60}^{2-})(NH_3)_3$, where M = Cd, Mn, Co, Zn, Ni, and Ba, were obtained in ammonia solutions and structurally characterized.[8—10] These salts are unstable at room temperature and decompose with loss of ammonia; probably, this is the reason why their properties have not been studied so far. The dianion C_{60}^{2-} was used as an intermediate in the synthesis of organoplatinum compounds in the presence of phosphorus-containing ligands.[11] At low temperatures, the dianion C_{60}^{2-} has a diamagnetic singlet ground state (S = 0), whereas the excited triplet state (S = 1) in some cases is populated only at near-room temperature.[12,13] Therefore, the onset of magnetic spin ordering or high conductivity in the salts containing metal cations and the dianions C_{60}^{2-} is unlikely. From the standpoint of conducting and magnetic materials design the synthesis of salts containing the radical anions $C_{60}^{\cdot-}$ is much more promising because these species have the spin state S = 1/2 and can therefore ensure magnetic exchange between paramagnetic centers. At the same time, a number of salts containing $C_{60}^{\cdot-}$ exhibit high metallic-type conductivity.[14—16] However, no solid fullerene salts containing the radical anions $C_{60}^{\cdot-}$ and d- or f-metal cations have been obtained so far. The interaction of C_{60} with anionic metal carbonyls including $(Cat^+)\{Co(CO)_4^-\}$, $(Cat^+)\{Mn(CO)_5^-\}$, and $(Cat^+)\{Re(CO)_5^-\}$ (cation Cat^+ = = Na^+ or PPN^+ (bis(triphenylphosphoraneylidene)ammonium)) in THF was studied.[17—19] It was assumed that initially the anionic metal carbonyls reduce C_{60} to $C_{60}^{\cdot-}$ and then the radicals $^{\cdot}M(CO)_{4(3)}$ formed in the reaction are η^2-coordinated to the fullerene anion to form ionic complexes $(Cat^+)\{M(CO)_{4(3)}(\eta^2\text{-}C_{60})^-\}$ (M = Co, Mn, Re). The crystal structure of the salt $(PPN^+)\{Mn(CO)_4(\eta^2\text{-}C_{60})^-\}$ was established.[19] Since the near-IR spectra of these

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compounds exhibit no absorption bands corresponding to $C_{60}^{\bullet-}$, it is believed that all salts contain a neutral fullerene and an anionic metal carbonylate.[17—19] Fullerene compounds with platinum group metals can be obtained as Pd_xC_{60} and Pt_xC_{60} films by electrochemical reduction of the Pd^{2+} and Pt^{2+} salts in the presence of C_{60}. Polymeric films M_xC_{60} contain neutral fullerenes and metals in the zero oxidation state.[20,21] Similar polymers M_xC_{60} (M = Pt, Pd) can be synthesized in the reactions of neutral fullerene with the coordination compounds of Pt(0) and Pd(0).[22,23]

In the present work, the interaction of the radical anions $C_{60}^{\bullet-}$ with divalent d- and f-metal (Co, Fe, Ni, Mn, Eu and Cd) cations in DMF and an acetonitrile—benzonitrile (AN—BN) mixture was studied for the first time. We have shown that the reactions in concentrated DMF solutions result in crystalline salts **1—6** containing the radical anions $C_{60}^{\bullet-}$ and metal(II) cations solvated by DMF. These salts were characterized by elemental analysis, as well as by the IR, near-IR, visible, and UV spectra, and by the EPR spectra in the temperature range 4—295 K. For two salts, magnetic measurements with a SQUID magnetometer were carried out. Strong magnetic interactions between fullerene anions and between the metal(II) cations in the salts were revealed. These methods were used to study polycrystalline precipitates obtained in the AN—BN mixture. A comparison of the properties of the compounds synthesized in DMF and the AN—BN mixture revealed significant differences between the reaction products of $C_{60}^{\bullet-}$ with metal(II) cations in these solvents.

Experimental

UV, visible, and near-IR spectra were recorded in KBr pellets on a Shimadzu-3100 spectrophotometer in the range 240—2600 nm. IR spectra were recorded in KBr pellets on a Perkin—Elmer 1000 spectrometer in the range 400—7800 cm^{-1} (resolution 1 cm^{-1}). EPR spectra were recorded on a JEOL JES-TE 200 X-band spectrometer equipped with a JEOL ES-CT470 cryostat in the temperature range 4—295 K. The magnetic properties of compounds **4** and **5** were studied with a Quantum Design MPMS-XL SQUID-magnetometer in the temperature range 1.9—300 K at 100 mT. The contribution of the sample holder and the diamagnetic contribution (χ_0) were subtracted from the experimental values The parameters C, θ, and χ_0 were calculated from the relation $\chi_M = C/(T - \theta) + \chi_0$ using experimental data for the molar magnetic susceptibility (χ_M) in the temperature range 15—150 K.

Compounds were synthesized from anhydrous metal salts MnI_2, $FeBr_2$, $CoBr_2$, NiI_2, $CdBr_2$, and EuI_2 (all purchased from Aldrich), C_{60} (purity 99.9%), and metallic cesium (Aldrich). Solvents were purified in argon atmosphere and vacuum distilled over molecular sieves (DMF, Aldrich), Na (benzonitrile), CaH_2 (*o*-dichlorobenzene), and over CaH_2, P_2O_5, and K_2CO_3 (acetonitrile). The solvents were degassed prior to use. All syntheses were carried out in an MBraun 150B-G box with inert atmosphere (H_2O and O_2 content less than 1 ppm). Compounds were stored in a box with inert atmosphere. The EPR and SQUID measurements were carried out in sealed quartz capillaries 2 mm in diameter. KBr pellets for spectral measurements in the IR, UV, visible, and near-IR regions were prepared under anaerobic conditions.

Synthesis of salts $(C_{60}^{\bullet-})_2\{(M^{2+})(DMF)_x\}$ (x = 2.4—4) (1—6) in DMF (general procedure). Fullerene C_{60} (100 mg, 0.1387 mmol) and metallic cesium (18.9 mg, 0.1387 mmol) were dissolved in 5 mL of DMF at 50 °C. After 6 h, the solution was cooled to ~20 °C. The near-IR spectrum of the solution corresponded to reduction of C_{60} to $C_{60}^{\bullet-}$, thus indicating the formation of the salt $(Cs^+)(C_{60}^{\bullet-})$ in the solution. To this solution. the metal(II) salt (0.1387 mmol) was added and stirred for 4 h at ~20 °C. Compounds **1** and **2** immediately precipitated as black powders. Salts **4—6** precipitated only partially. In these cases, 5 mL of AN were added to the solutions, which led to additional precipitation of black-brown substances. The precipitates were filtered off, washed with AN (5 mL), and dried at ~20 °C (yields were to 80% for **1** and **2** and 30—50% for **4—6**). The compositions of salts **1—6** can only approximately be determined from the elemental analysis data (Table 1) due to instability of the salts in air and oxidation in the course of elemental analysis. The oxidation of the radical anions $C_{60}^{\bullet-}$ can proceed as follows: $C_{60}^{\bullet-} + O_2 \rightarrow (C_{60} \cdot O_2^{-})$;[24] therefore, one can expect the addition of two oxygen molecules per formula unit of the sample, and the percentages of C, H, and N were calculated per system "formula unit + O_4". A similar situation was observed in the elemental analysis of most ionic compounds of C_{60}, which are unstable to oxidation.[25—27] The compositions of salts **1—6** listed in Table 1 were determined with allowance for optical spectroscopy data (see below).

Reaction products of $C_{60}^{\bullet-}$ with metal(II) salts (M = Fe, Mn, Co and Cd) in an AN—BN mixture. A mixture of C_{60} (50 mg, 0.0693 mmol) and metallic cesium (9.5 mg, 0.0693 mmol) was dissolved in 10 mL of BN at 50 °C. After 4 h, the solution was cooled to ~20 °C and filtered. Spectrophotometric measurements confirmed the reduction of C_{60} to $C_{60}^{\bullet-}$ and the formation of $(Cs^+)(C_{60}^{\bullet-})$ in the solution. The metal(II) salt (0.0693 mmol) was dissolved separately in 10 mL of AN and the solution thus

Table 1. Data from elemental analyses of salts **1—6**

Salt	$\frac{\text{Found}}{\text{Calculated}}$ (%)		
	C	H	N
$(C_{60})_2Co(DMF)_{3.3}$ (**1**)*	86.14	1.12	2.48
	86.42	1.28	2.56
$(C_{60})_2Ni(DMF)_4$ (**2**)	85.88	1.52	2.94
	86.47	1.40	2.80
$(C_{60})_2Fe(DMF)_4$ (**3**)**	84.93	1.75	2.83
	85.54	1.51	3.02
$(C_{60})_2Mn(DMF)_{3.5}$ (**4**)	85.62	1.61	2.77
	86.25	1.34	2.72
$(C_{60})_2Eu(DMF)_4$ (**5**)	78.89	1.93	2.92
	80.69	1.49	2.97
$(C_{60})_2Cd(DMF)_{2.5}$ (**6**)	86.36	1.13	1.82
	85.04	0.97	1.95

* Br content <0.7%.

** I content < 1.2%.

obtained was filtered into the solution of $(Cs^+)(C_{60}{}^{\bullet-})$. The solution thus obtained instantaneously bleached and a light-brown substance precipitated. The precipitate was filtered off, washed with AN (10 mL), and dried.

Results and Discussion

Syntheses in DMF and an AN—BN mixture. The salts **1—6** of the general formula $(C_{60}{}^{\bullet-})_2\{(M^{2+})(DMF)_x\}$ (x = 2.4—4) were synthesized under anaerobic conditions by the cation exchange reactions between $(Cs^+)(C_{60}{}^{\bullet-})$ and metal salts $M^{II}(Hal)_2$, (Hal = Cl, Br, I) in DMF. The salts **1—6** are poorly soluble in DMF compared to $(Cs^+)(C_{60}{}^{\bullet-})$ and precipitate from concentrated DMF solutions. All salts were obtained as black or black-brown powders. In pure AN, the salts slowly decompose (during a few hours) with the loss of DMF (according to the data from combustion analysis for nitrogen) and the black or black-brown precipitate turns light-brown; therefore, AN should not be used in excess when precipitating and washing the salts. The salts also decompose in other weakly coordinating solvents, *e.g.*, *o*-dichlorobenzene. Heating in *o*-$Cl_2C_6H_4$ causes gradual dissolution of the salts, followed by precipitation of light-brown powders upon the addition of AN; the powders are insoluble in DMF. Solid salts are stable under anaerobic conditions (no indications of decomposition were observed during a few months), their solutions in DMF are also stable for a long time. A 20-mg sample of the salt can completely be redissolved in 20 mL of DMF. This suggests no polymerization of $C_{60}{}^{\bullet-}$ in the salts on storage.

We failed to grow crystals of salts **1—6** suitable for X-ray studies. Slow diffusion (over a period of a month) of the solution of the metal salt in AN in the $(Cs^+)(C_{60}{}^{\bullet-})$ solution in DMF leads to poor-quality crystals and a large amount of light-brown precipitate in addition to crystals, which seems to be due to the decomposition of the salts in AN.

Reactions of the radical anions $C_{60}{}^{\bullet-}$ with metal(II) cations (M = Fe^{II}, Co^{II}, Cd^{II} and Mn^{II}) were also studied in the AN—BN mixture. The addition of the metal(II) salt solution in AN to the solution of $(Cs^+)(C_{60}{}^{\bullet-})$ in BN results in quantitative precipitation of a light-brown substance, which is insoluble in DMF, poorly soluble in CS_2 and benzene, but can be dissolved in $C_6H_4Cl_2$ on heating.

IR, UV, visible, and near-IR spectra. To determine the charge state of fullerene in the compounds synthesized, we studied their UV, visible, near-IR, and IR spectra. The spectra of salts **1—6** (Table 2) obey an identical pattern and here we will discuss the typical spectrum of only one salt, *viz.*, $(C_{60})_2Mn(DMF)_{3.5}$ (**4**). Fullerene C_{60} has four IR-active, symmetry-allowed modes corresponding to the absorption bands at 527, 577, 1182, and 1429 cm^{-1} (modes F_{1u}(1—4), respectively).[28] Only the mode F_{1u}(4) of C_{60} is sensitive to charge transfer to the fullerene molecule and the corresponding absorption band is shifted from 1429 cm^{-1} (neutral state) to 1395—1388 cm^{-1} (radical anion).[29,30] As to the compounds containing the dianions $C_{60}{}^{2-}$, this absorption band is at 1369 cm^{-1}.[13] In the spectrum of complex **1**, the absorption bands corresponding to the modes F_{1u}(1—4) of C_{60} are at 526, 575, 1182, and 1385 cm^{-1}, respectively (Fig. 1, *a*, arrows 1—4). Thus, the position of the absorption band corresponding to the mode F_{1u}(4) of C_{60} in the spectrum of **1** more likely characterizes the charge state of fullerene equal to −1. An increase in the intensity of the absorption band of the mode F_{1u}(2) at 575 cm^{-1} compared to that of the absorption band of the mode F_{1u}(1) at 526 cm^{-1} is also characteristic of negatively charged fullerene.[29,30] All spectra of the complexes exhibit a weak absorption band at 1432 cm^{-1} (see arrow 5 in Fig. 1, *a*). This band can be attributed to neutral fullerene (1429 cm^{-1}), but the solvent (DMF) as a constituent of the complex also has an absorption band in this region (at 1439 cm^{-1} for neat DMF). Therefore, the absorption band at 1432 cm^{-1} cannot unambiguously be assigned to fullerene. The UV, visible, and near-IR spectra of **1** are shown in Fig. 1, *b*. They exhibit two absorption bands at 948 and 1072 nm, which are characteristic of the radical anions $C_{60}{}^{\bullet-}$.[30] Salts **2—6** exhibit similar spectra with two absorption bands in the near-IR region (see Table 2). Thus, optical data indicate that the salts contain fullerene radical anions. Metal(II) cations have a charge of 2+; therefore, if the salts contain no halide anions, their compositions from the standpoint of electical neutrality should be 2 $(C_{60}{}^{\bullet-})$: (M^{2+}), which agrees with the results of elemental analysis of $(C_{60}{}^{\bullet-})_2\{(M^{2+})(DMF)_x$ (x = 2.4—4).

In addition to the absorption bands of fullerene anions, the spectrum shows intense absorption bands of DMF (see Fig. 1, *a* and Table 2). The C=O absorption band of the starting, unbound DMF (1680 cm^{-1}) is shifted to 1649—1659 cm^{-1} upon formation of salts **1—6**. It thus follows that the DMF molecules are coordinated to the metal(II) cations through the C=O groups. The spectra of salts **1—6** show no absorption bands except for those of the fullerene anions and DMF. It follows that at room temperature the fullerene anions form no dimers or polymers in the salts obtained, which would cause the appearance of new absorption bands in the spectra.[30,31]

If for some reasons (*e.g.*, with an excess of AN used for washing the salts) salts **1—6** undergo partial decomposition, the absorption band of neutral C_{60} at 1428 cm^{-1} appears in the IR spectrum and the intensities of the absorption bands at 526 and 575 cm^{-1} become equal. Thus, the absence of the absorption band at 1428 cm^{-1} in the IR spectrum and a higher intensity of the absorption band at 575 cm^{-1} compared to that of the band at 526 cm^{-1} (see Fig. 1, *a*) indicate a high purity of the salt obtained.

The UV, visible, near-IR, and IR spectra of the powders synthesized in the AN—BN mixture are similar to

Table 2. IR and near-IR spectra of systems under study

Compound	IR spectrum, ν/cm^{-1}		Near-IR region, λ/nm ($C_{60}^{\bullet-}$)
	$C_{60}^{\bullet-}$ and $(C_{60})_2$	DMF	
DMF	—	657, 1064, 1091, 1256, 1387, 1439, 1506, 1680	—
1	526, 575, 1182, 1383	660, 1061, 1089, 1257, 1383*, 1433, 1496, 1651	923, 1065
2	526, 576, 1182, 1383	660, 1062, 1089, 1256, 1383*, 1431, 1495, 1651	946, 1069
3	526, 575, 1182, 1385	660, 1061, 1107, 1257, 1385*, 1433, 1492, 1649	914, 1069
4	526, 575, 1182, 1385	661, 1059, 1105, 1253, 1385*, 1432, 1491, 1649	948, 1072
5	527, 575, 1180, 1385	670, 1060, 1100, 1255, 1385*, 1434, 1490, 1652	1072
6	526, 576, 1182, 1384	661, 1061, 1092, 1256, 1385*, 1432, 1492, 1659	917, 1064
$(Cs^+)(C_{60}^{\bullet-})$ + $FeBr_2$ (AN—BN)	526, 545, 576, 698, 735, 754*, 802, 1182, 1428, 1457	(BN) 685, 754*, 1145, 1489, 2224 **	—
$(C_{60})_2$[31]***	420, 479, 527, 549, 575, 612, 709, 726, 769, 796, 1186, 1426, 1462		—

* Absorption bands are overlapped.

** The spectrum also exhibits weak absorption bands at 922, 1024, and 1098 cm^{-1}, which cannot be assigned to $(C_{60})_2$ or BN.

*** Given for comparison.

one another irrespective of the metal. Figures 2, *a*, *b* show the spectra of the product isolated in the system ($(Cs^+)(C_{60}^{\bullet-})$ + $FeBr_2$) (see Table 2). They unambiguously indicate the neutral state of fullerene. Indeed, the C_{60} absorption bands corresponding to the mode $F_{1u}(4)$ are at 1427—1428 cm^{-1}, which is close to the absorption band at 1429 cm^{-1} in the spectrum of the starting fullerene. The absorption band at 575 cm^{-1} corresponding to the mode $F_{1u}(2)$ is much weaker than the band at 525 cm^{-1} corresponding to the mode $F_{1u}(1)$, which is also characteristic of neutral fullerene. The near-IR spectrum exhibits no absorption band of the radical anions $C_{60}^{\bullet-}$ (see Fig. 2, *b*). Note that fullerene formed in the reaction is not a starting monomeric fullerene; most probably, it is a neutral dimer $(C_{60})_2$. This also follows from poor solubility of the light-brown precipitate in CS_2 and benzene, whereas C_{60} is well soluble in these solvents. At the same time both the precipitate and the dimer $(C_{60})_2$ are soluble in *o*-$Cl_2C_6H_4$.[31] Yet another proof of dimer formation is provided by the appearance of a large number of new absorption bands in the IR spectrum (see Fig. 2, *a* and Table 2). Among them, the strongest bands are also characteristic of the IR spectrum of the dimer $(C_{60})_2$ [31] (see Table 2).

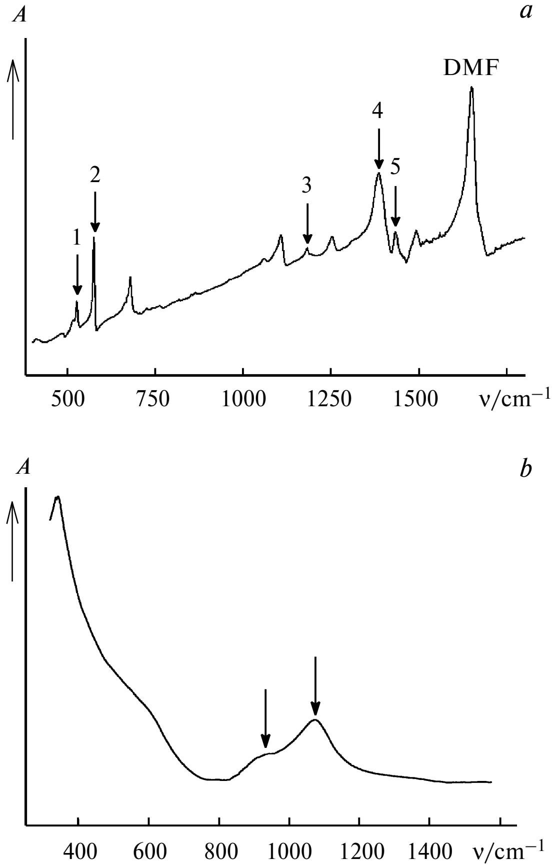

Fig. 1. IR (*a*), UV, visible, and near-IR (*b*) spectra of salt $(C_{60}^{\bullet-})_2\{(Mn^{2+})(DMF)_{3.5}\}$ (**1**) at $T = 293$ K.

Magnetic properties of salts 1—6 synthesized in DMF. The magnetic properties of salts **1**—**6** were studied by EPR spectroscopy in the temperature interval from 4 to 295 K. The EPR spectral parameters at 295 and 4 K are listed in Table 3.

The EPR spectrum of salt **1** at 295 K exhibits an intense signal with $g = 1.9951$ and the width $\Delta H = 5.65$ mT (Fig. 3, *c*, *d*). Based on these parameters, the signal can be assigned to the radical anion $C_{60}^{\bullet-}$, which is characterized by the *g*-factor in the range 1.996—1.999 (ΔH = = 2—6 mT).[3,30] Usually, the EPR signals of ionic compounds of C_{60} become considerably narrower as the temperature decreases and become no wider than 0.5 mT at $T < 150$ K.[3,32—35] Note that the EPR signal of the molecu-

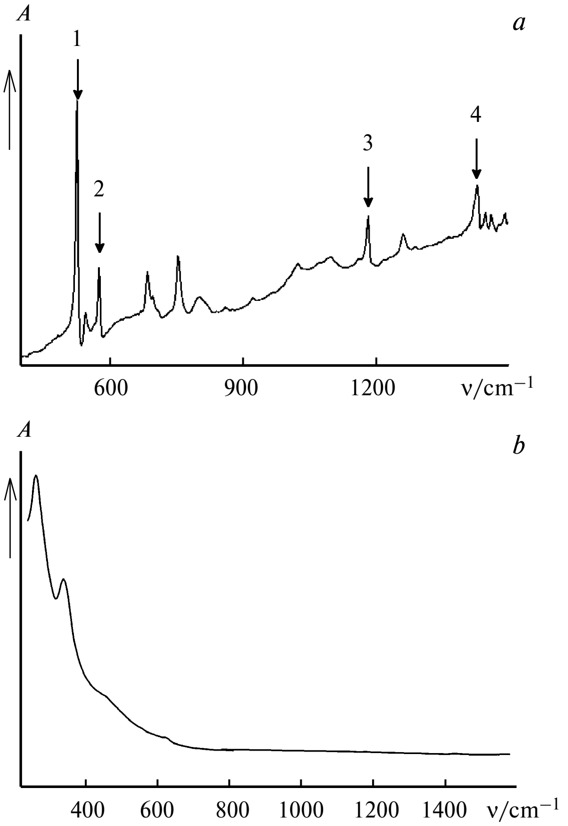

Fig. 2. IR (*a*) and UV, visible, and near-IR (*b*) spectra of the product precipitated from the AN—BN mixture in the reaction of $(Cs^+)(C_{60}{}^{\bullet -})$ with $FeBr_2$; $T = 293$ K.

lar ferromagnetic TDAE•C_{60} (TDAE is tetrakis(dimethylamino)ethylene) has a witdth of 2.2 mT at room temperature and narrows as the temperature decreases; a noticeable broadening of the signal is only observed upon transition of the compound to the ferromagnetic state at $T < 16$ K.[35] However, the EPR signal of salt **1** retains its width (5.6 mT) as the temperature decreases. Signal broadening begins at $T < 100$ K and continues up to a maximum width of 35.65 mT at 5 K (Fig. 3, *d*). The so broad EPR signals were for the first time observed for the salts containing the radical anions $C_{60}{}^{\bullet -}$. The *g*-factor of the EPR signal of salt **1** weakly depends on temperature up to 100 K but undergoes a significant shift toward smaller values at $T < 100$ K ($g = 1.9850$ at 6 K, see Fig. 3, *c*). The integrated intensity of the signal increases as the temperature decreases, reaches a maximum value at 5 K, and then decreases (Fig. 3, *b*). This behavior can be associated with the antiferromagnetic spin-spin interaction between $C_{60}{}^{\bullet -}$. No EPR signal of the cation Co^{2+} was observed at room temperature, probably because it is very broad. At 100 K, a broad signal with $g = 4.4024$ and $\Delta H = 134$ mT appears in the spectrum; it can be assigned to the high-spin state of the cation Co^{2+} ($S = 3/2$).[36,37] As the temperature is lowered to 38 K, the signal narrows to 42.2 mT, becomes asymmetrical, and then splits into three components with $g_1 = 4.8664$ ($\Delta H = 26.2$ mT), $g_2 = 4.1645$ ($\Delta H = 29.2$ mT), and $g_3 = 3.7337$ ($\Delta H = 27.4$ mT) at 4 K (see Fig. 3, *a*). The integrated intensities of this signal and its components increase as the temperature decreases, but exhibit an abrupt, more than twofold decrease at $T < 9$ K. This suggests that not only the radical anions $C_{60}{}^{\bullet -}$, but also cations Co^{2+} are involved in antiferromagnetic spin-spin interaction.

The EPR spectrum of salt **2** at 295 K exhibits a signal of $C_{60}{}^{\bullet -}$ ($g = 1.9918$, $\Delta H = 12.6$ mT). No EPR signal of the cations Ni^{2+} was observed.[38] As the temperature decreases, the EPR signal of $C_{60}{}^{\bullet -}$ behaves just like the signal in

Table 3. Parameters of EPR signals of salts **1—6** at 295 and 4 K

Compound	*g*-Factor (ΔH/mT)			
	$T = 295$ K		$T = 4$ K	
	M^{2+}	$C_{60}{}^{\bullet -}$	M^{2+}	$C_{60}{}^{\bullet -}$
1	—	1.9951 (5.65)	4.8664 (26.2) 4.1645 (29.2) 3.7337 (27.4)	1.9922 (30.9)
2	—	1.9918 (12.6)	—	1.9851 (34.2)
3	—	1.9954 (7.98)	—	1.9651 (9.85)
4	2.1390 (15.6) 2.0806 (27.8) 1.8755 (19.8)	1.9957 (19.8)	2.0815 (15.2) 2.0275 (36.2) 1.8848 (23.2)	—
5	*	1.9963 (7.88)	*	**
6	—	1.9988 (3.40)	—	1.9973 (0.32)

* EPR signal of the cation Eu^{2+} in the spectrum of salt **5** is observed at both room temperature (295 K) and 4 K; however, we failed to determine the *g*-factor of the signal.

** A very weak signal of $C_{60}{}^{\bullet -}$ is observed, corresponding to at most 0.5% of the overall content of C_{60}.

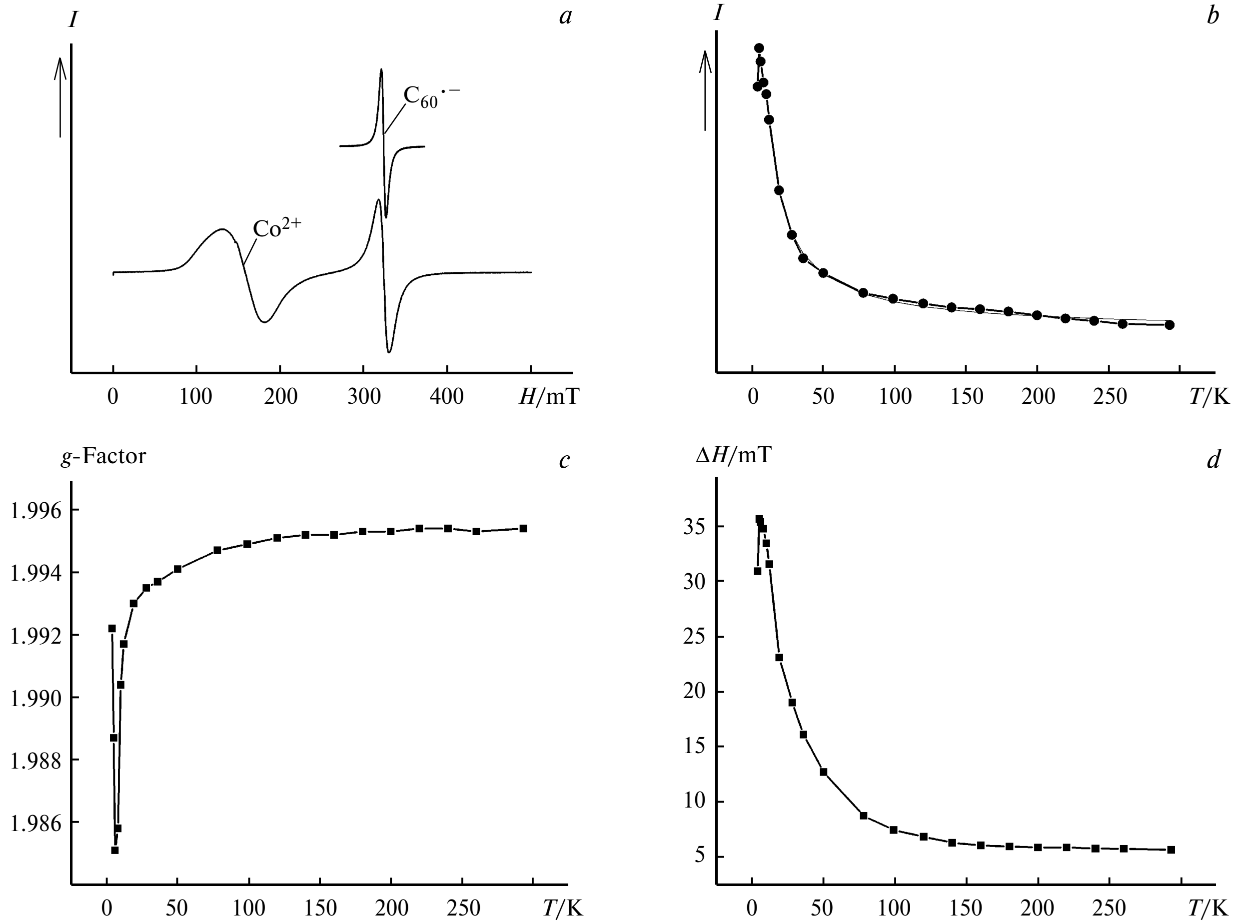

Fig. 3. EPR spectra of salt **1** at 295 and 4 K (*a*). The integrated intensity (*b*), *g*-factor (*c*), and width (*d*) of the EPR signal of $C_{60}^{\bullet-}$ plotted *vs*. temperature. The line in Fig. 3, *b* denotes the approximation of the experimental data using the Curie—Weiss law with the Weiss temperature of –3 K.

the spectrum of **1**, but the signal of **2** is even more broadened (to 40.1 mT at 6 K) and the *g*-factor is shifted toward smaller values (to 1.9721 at 10 K).

The magnetic behavior of salt **3** is similar. The EPR signal of $C_{60}^{\bullet-}$ is characterized by $g = 1.9954$ ($\Delta H = 7.98$ mT) at 295 K (Fig. 4, *b*, *c*). As for salt **2**, no indications of the cation Fe^{2+} were observed in the EPR spectra.[38] Unlike salts **1** and **2**, the EPR signal in the spectrum of **3** at $T < 295$ K slightly narrows as the temperature decreases, being broadened only at $T < 100$ K (Fig. 4, *c*). As a result, at low temperatures the signal in the spectrum of salt **3** is three- or fourfold narrower than the signals in the EPR spectra of **1** and **2** ($\Delta H = 10.37$ mT at 6 K). Other changes in the EPR parameters of the signal of $C_{60}^{\bullet-}$ of salt **3** on lowering the temperature are similar to those reported for **1** and **2** (see Fig. 4).

The Weiss temperatures calculated using the Curie—Weiss law from the temperature dependences of the integrated intensities of the EPR signals of $C_{60}^{\bullet-}$ in the range 20—300 K are –3 K for **1** (see Fig. 3, *b*), –24 K for **2**, and –19 K for **3** (see Fig. 4, *a*). This suggests rather strong antiferromagnetic interactions between $C_{60}^{\bullet-}$ spins in salts **2** and **3** and weaker spin interactions in salt **1**. No correlation between the signal width at low temperatures and the Weiss temperature was established. Probably, other processes, *e.g.*, the exchange interaction with paramagnetic metal(II) cations also contribute to the signal broadening.

Salt **4** exhibits a complex EPR spectrum at 295 K (Fig. 5, *a*), which can be represented as a superposition of Lorentzian components (see Table 3). One of them, characterized by $g_3 = 1.9957$ and $\Delta H = 19.8$ mT, corresponds to $C_{60}^{\bullet-}$. The other three components with $g_1 = 2.1390$ ($\Delta H = 15.6$ mT), $g_2 = 2.0806$ ($\Delta H = 27.8$ mT), and $g_4 = 1.8755$ ($\Delta H = 19.8$ mT) are attributed to asymmetrical signal of Mn^{2+}.[38] At $T < 200$ K, the intensity of the component corresponding to $C_{60}^{\bullet-}$ begins to decrease and this component becomes almost indistinguishable against the background of the intense signal of Mn^{2+} at $T < 150$ K. This is clearly seen in the spectrum recorded at 4 K (Fig. 5, *a*). Thus, the EPR data point to disappearance of the $C_{60}^{\bullet-}$ spins in salt **4** at 200—150 K, which can be due to dimerization of the radical anions $C_{60}^{\bullet-}$ and formation of dia-

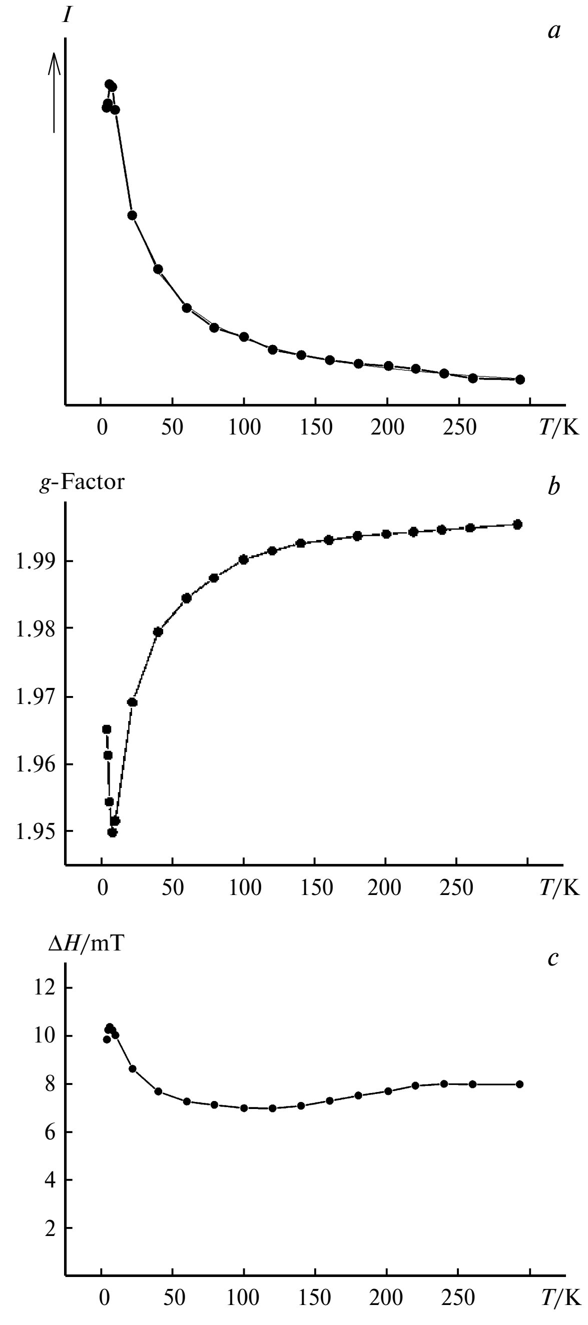

Fig. 4. The integrated intensity (*a*), *g*-factor (*b*), and width (*c*) of the EPR signal of the radical anion $C_{60}{}^{\bullet-}$ in $(C_{60}{}^{\bullet-})_2\{(Fe^{2+})(DMF)_4\}$ (**3**) plotted *vs.* temperature. The line in Fig. 4, *a* denotes the approximation of the experimental data using the Curie—Weiss law with the Weiss temperature of –19 K.

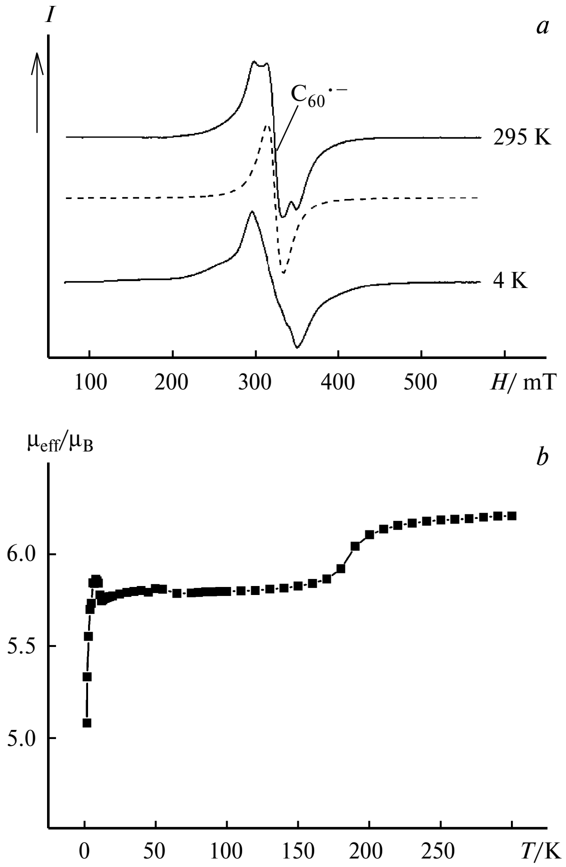

Fig. 5. (*a*) EPR spectra of salt $(C_{60}{}^{\bullet-})_2\{(Mn^{2+})(DMF)_{3.5}\}$ (**4**) at 295 and 4 K. Dashed line denotes one of the four Lorentzian spectral components assigned to $C_{60}{}^{\bullet-}$. (*b*) The magnetic moment of **4** plotted *vs.* temperature in the range 1.9—300 K.

magnetic dimers $(C_{60}{}^{-})_2$ linked by a C—C bond.[27,39–42] To confirm these assumptions, the magnetic properties of salt **4** were studied with a SQUID magnetometer (see Fig. 5, *b*). The magnetic moment of this salt is 6.21 μ_B per formula unit at 300 K, which is close to a value of 6.40 μ_B calculated for the system of three noninteracting spins $S = 5/2 + 1/2 + 1/2$ ($S = 5/2$ for the high-spin state of Mn^{2+} and $S = 1/2$ for the spin state of $C_{60}{}^{\bullet-}$). At $T < 210$ K, the magnetic moment of the salt begins to decrease and reaches a value of 5.81 μ_B at 150 K (see Fig. 5, *b*), which is close to the value 5.91 μ_B, calculated for the system with one noninteracting spin $S = 5/2$ (this is characteristic of Mn^{2+} in the high-spin state). Dimerization is typical of the ionic compounds of fullerenes characterized by short contacts between radical anions $C_{60}{}^{\bullet-}$ and is observed in the temperature interval 150—250 K.[26,39–42] At $T < 150$ K, the magnetic susceptibility is determined by the spins localized on Mn^{2+} and obeys the Curie—Weiss law with a nearly zero Weiss temperature in the temperature range 15—150 K. Thus, the formation of diamagnetic dimers $(C_{60}{}^{-})_2$ leads to magnetic isolation of the cations Mn^{2+}.

Dimerization of the radical anions $C_{60}{}^{\bullet-}$ in salt **5** can immediately be observed by EPR spectroscopy because the EPR signals of $C_{60}{}^{\bullet-}$ and the cation Eu^{2+} have different parameters. The signal of $C_{60}{}^{\bullet-}$ is characterized by $g = 1.9963$ and $\Delta H = 7.88$ mT at 295 K (Fig. 6, *c*). The multiplet observed in the whole range of magnetic fields from –100 to 700 mT is attributed to the cation Eu^{2+}. The multiplet includes a large number of components separated by 54.8 to 82.5 mT. These lines can be due to the splitting at the Eu^{2+} nucleus ($I = 7/2$). The signal of Eu^{2+} is observed down to 4 K (Fig. 6, *d*). As the temperature decreases, the integrated intensity of the signal of $C_{60}{}^{\bullet-}$ decreases in the temperature range 170—130 K (see Fig. 6, *b*) and at $T < 100$ K it corresponds to the contribution of less than 0.5% of spins of the total number of the C_{60} molecules. The weak signal of $C_{60}{}^{\bullet-}$ is observed down to 4 K (see Fig. 6, *d*). These data unambiguously indicate the dimerization of the radical anions $C_{60}{}^{\bullet-}$ in the temperature range 170—130 K. The magnetic moment of the complex equal to 7.12 μ_B at 300 K decreases at $T < 180$ K to a value of 6.85 μ_B ($T = 130$ K). This behavior is in good agreement with the scheme of transition from the system of three noninteracting spins ($S = 7/2 + 1/2 + 1/2$) to the system with only one noninteracting spin $S = 7/2$ (Eu^{2+}). Thus, the contribution of the radical anions $C_{60}{}^{\bullet-}$ to the magnetic susceptibility vanishes at 180—130 K; this agrees with the EPR spectroscopy data. The magnetic susceptibility of compound **5** in the temperature range 15—140 K obeys the Curie—Weiss law with almost zero Weiss temperature. As can be seen, the formation of diamagnetic dimers $(C_{60}{}^{-})_2$ for both **5** and **4** excludes magnetic exchange between the cations Eu^{2+}.

Replacement of paramagnetic metal cations in salts **1—3** by a diamagnetic cation Cd^{2+} (salt **6**) fundamentally changes the magnetic properties of this system. The EPR spectrum of salt **6** at 295 K exhibits the EPR signal of $C_{60}{}^{\bullet-}$ with $g = 1.9988$ ($\Delta H = 3.4$ mT). Lowering the temperature causes a significant narrowing of the signal to $\Delta H = 0.32$ mT at 4 K (Fig. 7, *c*) and is also accompanied by a small (compared to the spectra of salts **1—3**) shift of the *g*-factor toward smaller values (Fig. 7, *b*) and by an increase in the integrated intensity of the signal down to 4 K (see Fig. 7, *a*) with no maximum at 5—6 K, as was observed for salts **1—3**. This behavior can be due to magnetic isolation of the radical anions $C_{60}{}^{\bullet-}$. Usually, the manifestation of magnetic interaction in ionic compounds of fullerenes at low temperatures causes a significant broadening of the EPR signal of $C_{60}{}^{\bullet-}$ and a shift of the *g*-factor,[32,33,35,42,43] which is not observed for salt **6**. The Weiss temperature determined from the temperature dependence of the integrated intensity of the EPR signal of $C_{60}{}^{\bullet-}$ in the temperature range 20—300 K equals only −0.4 K, which also agrees with

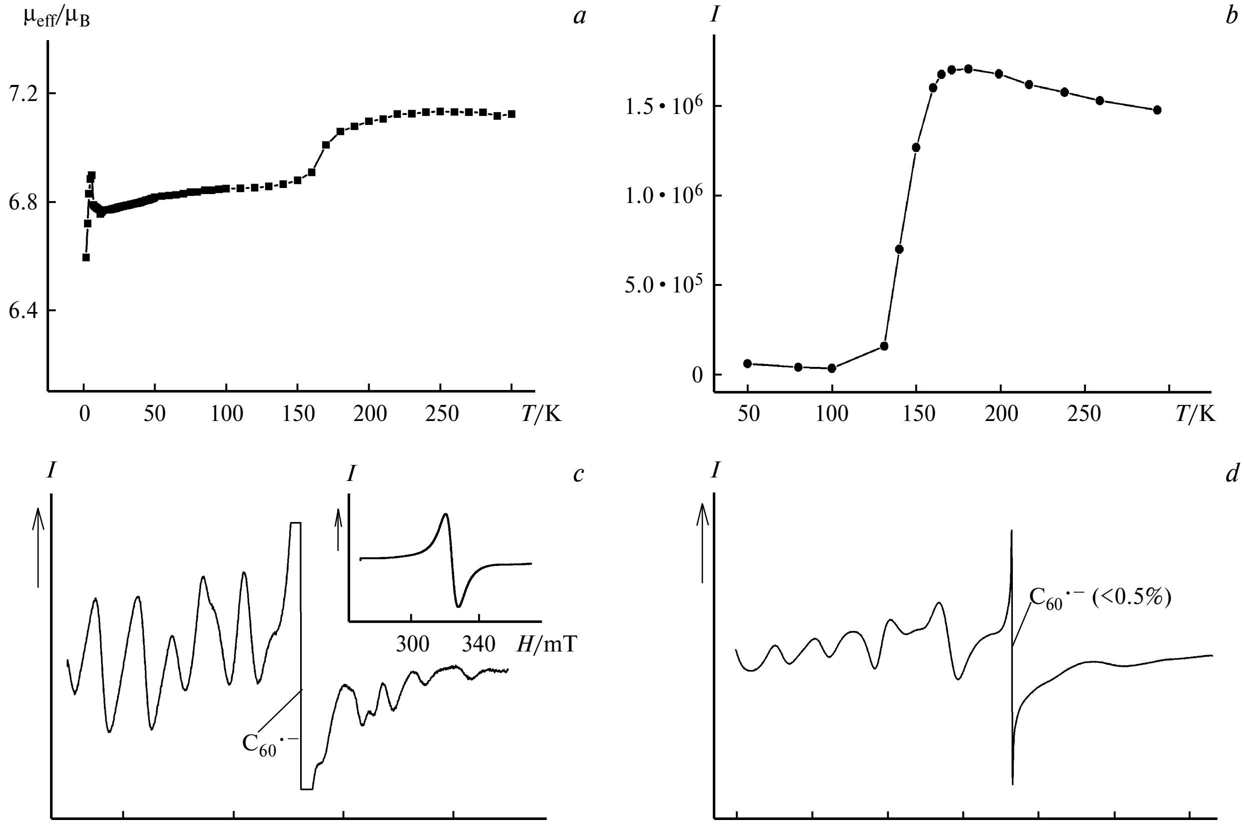

Fig. 6. The magnetic moment of $(C_{60}{}^{\bullet-})_2\{(Eu^{2+})(DMF)_4\}$ (**5**) plotted vs. temperature in the range 1.9—300 K (*a*); the integrated intensity of the EPR signal of the radical anion $C_{60}{}^{\bullet-}$ plotted vs. temperature in the range 50—295 K (*b*); and the EPR spectra of salt **5** at 295 (*c*) and 4 K (*d*) at magnetic fields from 100 to 700 mT. Inset: in Fig. 6, *c*: EPR signal of $C_{60}{}^{\bullet-}$.

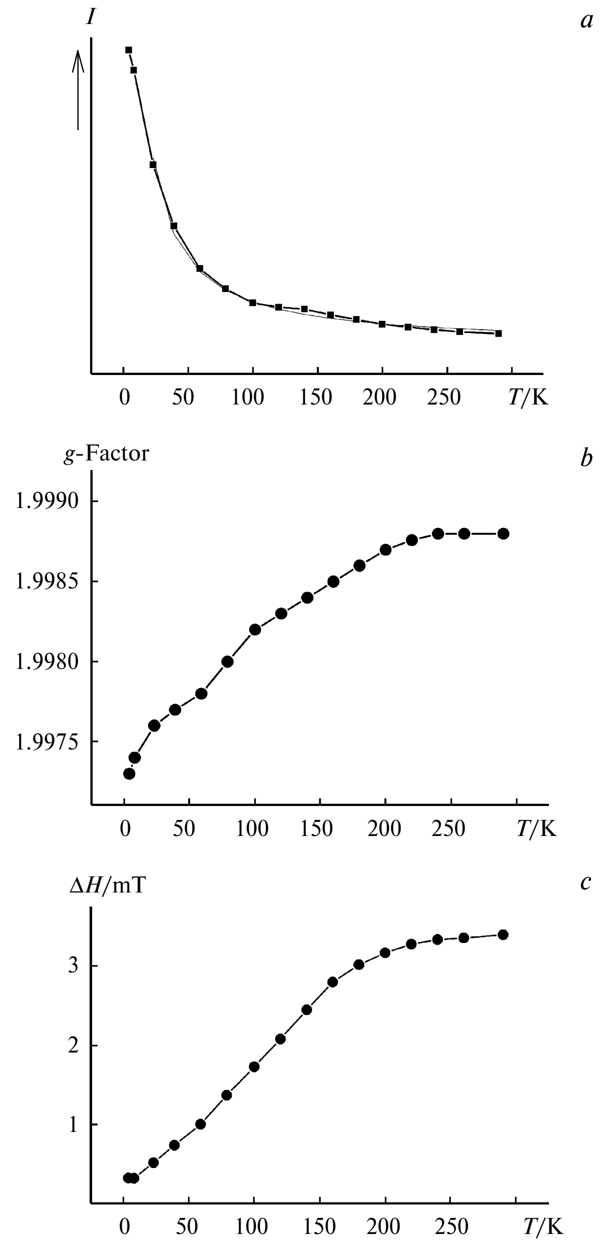

Fig. 7. The integrated intensity (*a*), *g*-factor (*b*), and linewidth (*c*) of the EPR signal of the radical anion $C_{60}{}^{\bullet-}$ in $(C_{60}{}^{\bullet-})_2\{(Cd^{2+})(DMF)_{2.5}\}$ (**6**) plotted *vs*. temperature. The line in Fig. 7, *a* denotes the approximation of the experimental data using the Curie—Weiss law with the Weiss temperature of –0.4 K.

the lack of magnetic interaction between the radical anions $C_{60}{}^{\bullet-}$.

EPR studies of the interaction products of the radical anions $C_{60}{}^{\bullet-}$ with metal cations in the AN—BN mixture. The EPR spectra of the reaction products of the radical anions $C_{60}{}^{\bullet-}$ with metal cations in the AN—BN mixture (Table 4) show two types of signals. The signals with $g = 1.9998$—1.9990 are attributed to $C_{60}{}^{\bullet-}$. They are very weak and manifest themselves only at low temperatures. In all cases, the contribution of $C_{60}{}^{\bullet-}$ is at most 0.1—0.3% of the total number of the C_{60} molecules (calculated with respect to the total amount of the starting C_{60}). These data confirm the results of analysis of the optical spectra, according to which the reactions afford neutral fullerenes.

The EPR spectra of the products formed in the reactions of $C_{60}{}^{\bullet-}$ with paramagnetic cations Co^{2+}, Fe^{2+}, and Mn^{2+} exhibit strong EPR signals of the metals (see Table 4). These spectra are significantly different from those of the starting metal salts ($FeBr_2$ and $CoBr_2$ give no EPR signals, while the signal of MnI_2 is characterized by $g = 2.017$ and $\Delta H = 44.7$ mT at 295 K) and the EPR spectra of the metal(II) cations in salts **1**, **3**, and **4**. Since in the reaction under study the radical anions $C_{60}{}^{\bullet-}$ are oxidized to neutral C_{60}, the oxidation states of the metals should also decrease from +2 to +1 or 0. Since the IR spectra of these products exhibit the absorption band of BN, one can assume that the metals solvated by benzonitrile also precipitate from the corresponding solutions along with neutral fullerene. Recrystallization of the products obtained from *o*-$Cl_2C_6H_4$ under anaerobic conditions causes a considerable decrease in the intensity of the EPR signal of the metal and disappearance of this signal after two or three recrystallizations. After the first recrystallization of the product from *o*-$Cl_2C_6H_4$, the EPR signal of the metal was also observed in the mother solution. This is probably due to partial dissolution of the metal solvated by benzonitrile in *o*-$Cl_2C_6H_4$.

Specific features of the interaction of $C_{60}{}^{\bullet-}$ with metal cations. Thus, the results obtained point to significant differences the reaction products of the radical anions $C_{60}{}^{\bullet-}$ with divalent metal cations in DMF and in the AN—BN mixture. The reactions in DMF result in the salts **1—6** containing the radical anions $C_{60}{}^{\bullet-}$ and metal(II) cations solvated by DMF:

$$(Cs^+)(C_{60}{}^{\bullet-}) + M^{2+} \rightarrow (C_{60}{}^{\bullet-})_2\{(M^{2+})(DMF)_x\}$$

$(x = 2.4$—$4)$.

Only neutral products are obtained in the AN—BN mixture. Moreover, the salts $(C_{60}{}^{\bullet-})_2\{(M^{2+})(DMF)_x\}$ decompose in AN or *o*-$Cl_2C_6H_4$ with the loss of DMF and formation of neutral fullerene. It should be noted that the coordinating ability of DMF is much higher than those of AN and BN. The donor number* of DMF is 26.6 (*cf.* 14.1 for AN and 11.9 for BN).**[44]** One can assume that the decomposition of the salts occurs through coordination of the radical anions $C_{60}{}^{\bullet-}$ to the metal(II) cation. Strongly coordinating solvents go to the coordination sphere of the metal(II) cation, thus precluding coordination of $C_{60}{}^{\bullet-}$ to the metal and making the salts stable in these solvents.

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* The donor number (DN) is defined as the $-\Delta H_0$ of the reaction of the solvent with $AsCl_5$ in an inert solvent (1,2-dichloroethane).

Table 4. EPR spectral parameters of products synthesized in the AN—BN mixture

Reaction	*g*-Factor (ΔH/mT)			
	$T = 295$ K		$T = 4$ K	
	M^{2+}	$C_{60}{}^{\bullet-}$*	M^{2+}	$C_{60}{}^{\bullet-}$*
$(Cs^+)(C_{60}{}^{\bullet-}) + MnI_2$	2.021 (66.0)	—	—	1.9994 (0.33)
$(Cs^+)(C_{60}{}^{\bullet-}) + FeBr_2$	2.074 (65.2)	—	3.360 (172.0)	1.9992 (0.45)
$(Cs^+)(C_{60}{}^{\bullet-}) + CdBr_2$	—	1.9998 (1.85)	—	1.9994 (0.32)
$(Cs^+)(C_{60}{}^{\bullet-}) + CoBr_2$	2.260 (95.0)	—	—	1.9990 (0.36)
	2.157 (24.2)	—	2.147 (22.2)	

* In all cases, the intensity of the EPR signals of the radical anion $C_{60}{}^{\bullet-}$ is very low and corresponds to the contribution of at most 0.1—0.3% spins of the total number of C_{60} molecules.

Displacement of a weakly coordinating solvent by $C_{60}{}^{\bullet-}$ from the coordination sphere of the metal is followed by the formation of an intermediate coordination compound $(C_{60}{}^{-})_2(M^{2+})$ characterized by redistribution of the electron density between $C_{60}{}^{-}$ and M^{2+} and subsequent formation of neutral fullerene and a decrease in the oxidation state of the metal. For instance, in the salts $(Cat^+)\{M(CO)_{4(3)}(\eta^2\text{-}C_{60})^-\}$ (M = Co, Mn and Re) the negative charge is mainly localized on the metal after η^2-coordination of anionic metal carbonyl to fullerene, while fullerenes become almost neutral.[17—19] The coordination compound $(C_{60}{}^{-})_2(M^{2+})$ is unstable and decomposes in solution to a neutral fullerene dimer and the metal solvated by BN. The formation of neutral fullerene as a result of the oxidation of the radical anions $C_{60}{}^{\bullet-}$ by the metal(II) cations without coordination to the metal seems to be impossible because the redox potentials of the cations M^{2+} in polar solvents are much more negative (*e.g.*, $E^{2+/0}$ of Mn^{2+}, Co^{2+} and Fe^{2+} are less than -1.3 V *vs.* s.c.e. in DMF)[45] than the oxidation potential of $C_{60}{}^{\bullet-}$ ($E^{0/-} = -0.26$ V *vs.* s.c.e in DMF).[46] The formation of the dimer $(C_{60})_2$ in the decomposition of this salt can be related to the structure of the unstable intermediate $(C_{60}{}^{-})_2(M^{2+})$ in which the metal cation is coordinated to two fullerene radical anions. Decomposition of this intermediate will give two C_{60} molecules with activated π-bonds, which favors dimerization of C_{60}. The formation of the dimer $(C_{60})_2$ from neutral C_{60} activated by, *e.g.*, KCN was observed earlier.[31] Thus, the reaction in the AN—BN mixture can be described as follows:

$$(Cs^+)(C_{60}{}^{\bullet-}) + M^{2+} \rightarrow (C_{60}{}^{-})_2(M^{2+})(BN)_x \rightarrow$$
$$\rightarrow (C_{60})_2\{M(BN)_x\} \rightarrow (C_{60})_2 + M(BN)_x.$$

Thus, we have shown that reactions of the radical anions $C_{60}{}^{\bullet-}$ with divalent metal cations in DMF and in the AN—BN mixture result in significantly different products. The reactions in DMF result in salts **1—6** of the general formula $(C_{60}{}^{\bullet-})_2\{(M^{2+})(DMF)_x\}$ ($x = 2.4$—4), comprising the radical anions $C_{60}{}^{\bullet-}$ and metal(II) cations solvated by DMF. The reactions in the AN—BN mixture afford only neutral products of decomposition of these salts.

Salts containing fullerene radical anions and paramagnetic cations of divalent d- and f-metals have been obtained for the first time. Earlier,[15,16,27,47] only salts containing fullerene radical anions and diamagnetic alkali metal cations solvated by DMF or THF have been known. The ionic character of the ground state of salts **1—6** was substantiated by the IR, near-IR, and EPR spectra. Based on the magnetic behavior, salts **1—6** can be divided into three groups. In the salts **1—3** containing the cations Co^{2+}, Ni^{2+}, and Fe^{2+} no dimerization of the radical anions $C_{60}{}^{\bullet-}$ occurs down to the lowest temperatures (4 K). Nonzero spins of both fullerene and M^{2+} give rise to antiferromagnetic interactions between the radical anions $C_{60}{}^{\bullet-}$ (particularly strong interactions were revealed for the salts containing Ni^{2+} and Fe^{2+}), but the metal cations can also be involved, as shown by the Co^{2+}-containing salt as an example. However, it should be emphasized that these antiferromagnetic interactions seem to be of short-range nature since no long-range antiferromagnetic spin ordering is observed in these salts down to 4 K.

The second group includes salts **4** and **5** containing the cations Mn^{2+} and Eu^{2+}, respectively. The EPR spectra of these salts exhibit signals of the radical anions $C_{60}{}^{\bullet-}$ and metal(II) cations, but unlike compounds **1—3**, the spins of the radical anions $C_{60}{}^{\bullet-}$ disappear at 210—130 K owing to formation of diamagnetic dimers $(C_{60}{}^{-})_2$. This is accompanied by disappearance of the EPR signal of $C_{60}{}^{\bullet-}$ and by a decrease in the magnetic moment of the complex. The dimerization is reversible, and dimers dissociate into the starting radical anions $C_{60}{}^{\bullet-}$ on heating to above 130—210 K. After dimerization, the spins localized on the cations Mn^{2+} and Eu^{2+} are magnetically isolated because the metal cations can be separated in space by the diamagnetic dimers $(C_{60}{}^{-})_2$. A similar situation was observed in ionic complexes of fullerene with metallocenes (here, dimerization of $C_{60}{}^{\bullet-}$ leads to magnetic isolation of paramagnetic metallocene cations by diamagnetic dimers $(C_{60}{}^{-})_2$ and $(C_{70}{}^{-})_2$).[27]

The third group includes salt **6**, which contains a diamagnetic cation Cd^{2+}. The behavior of this salt suggests magnetic isolation of the radical anions $C_{60}{}^{\bullet-}$ by the diamagnetic cations $(Cd^{2+})(DMF)_{2.5}$.

Thus, the manifestation of the magnetic interaction in these salts requires nonzero spins of both fullerene and metal(II) cation. Diamagnetic species (dimer $(C_{60}{}^{-})_2$, $Cd^{2+}(DMF)_{2.5}$) perturb the magnetic interaction.

In the future, we plan to study the conducting properties of salts **1—6**. Since their conductivities are due to the presence of the radical anions $C_{60}{}^{\bullet-}$ whose spins are involved in antiferromagnetic interactions, one can expect the magnetic field effect on the conductivity of these systems.

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